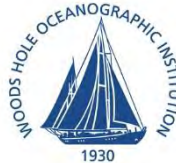


# Air Quality Implications of Crude Oil Evaporation

## New Insights from Bottom-Up Modeling



**Greg Drozd, David Worton, Haofei Zhang,**  
Christoph Aeppli Chris Reddy, Allen Goldstein

# Oil Spills



# Oil Spills

## Environmental Effects

**Land**



**Sea**



**Air**

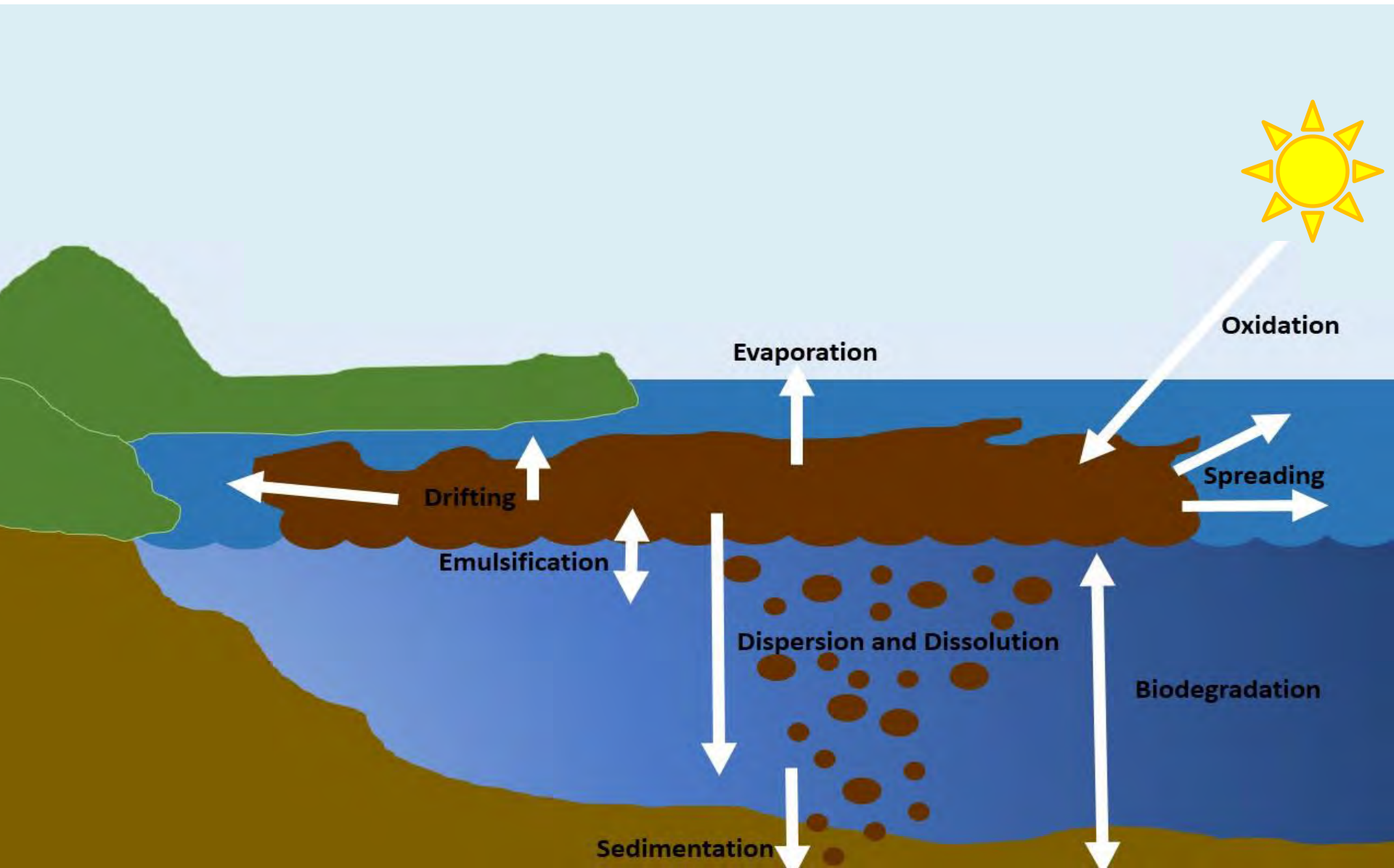


# Outline

- 1. The fate of spilled oil**
- 2. Atmospheric pollutant formation from the Deepwater Horizon (DWH) disaster**
- 3. Evaporation modeling**
- 4. Comprehensive composition measurements of oil**
- 5. Applications of evaporation model**
  - a. How is released oil transported?
  - b. How much and what type of aerosol is formed?

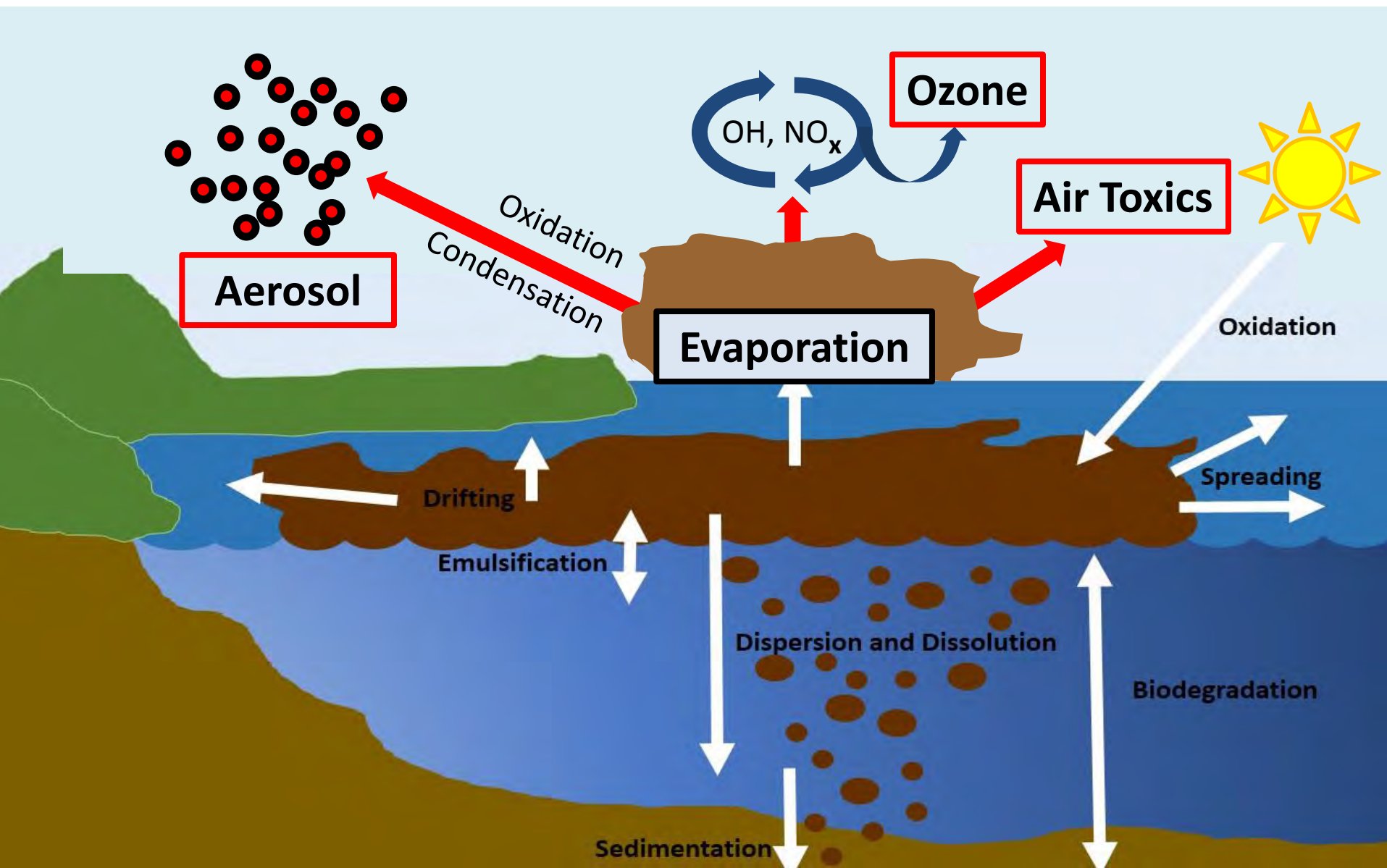
# Oil Spills

## Fate of Oil

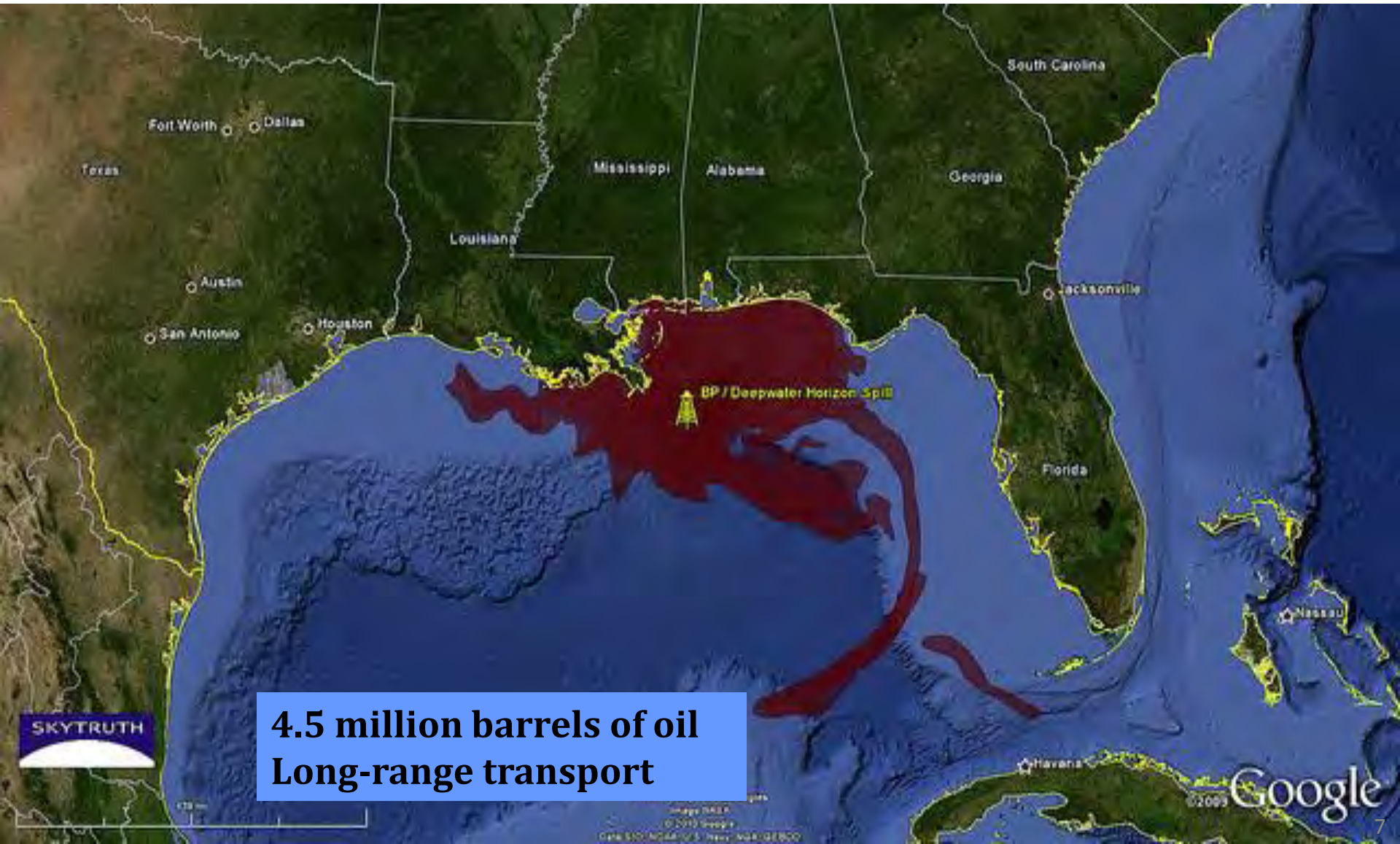


# Oil Spills

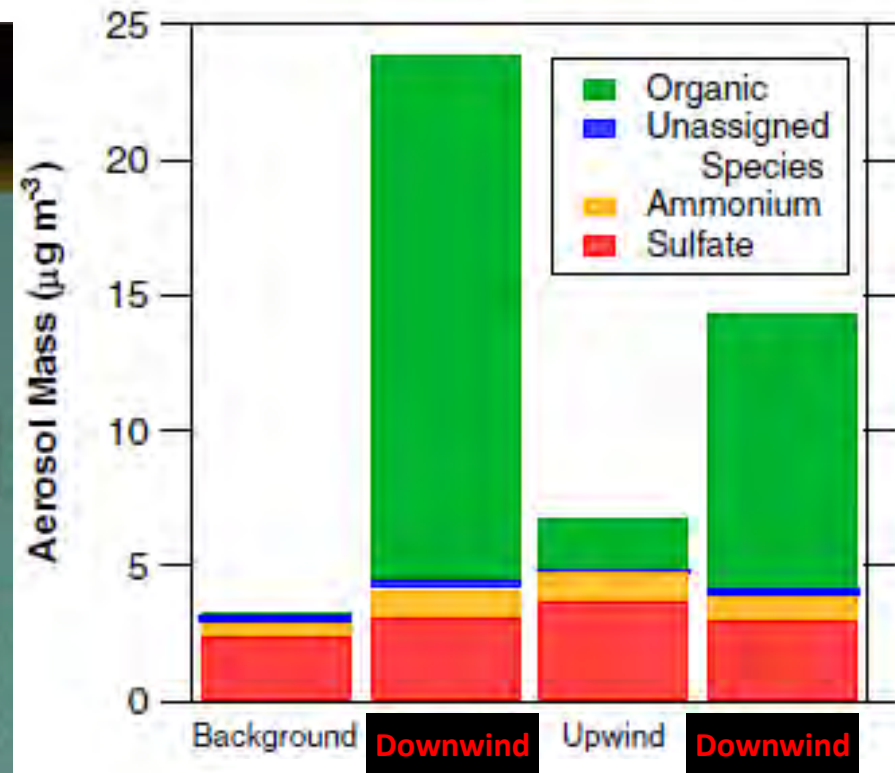
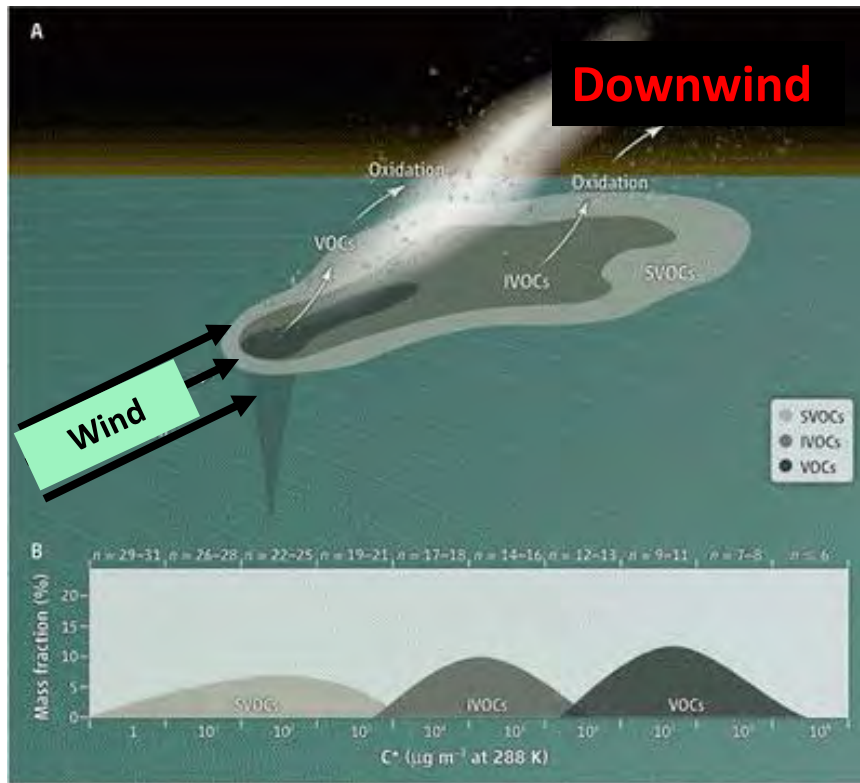
## Pollutant Formation



# Deepwater Horizon (DWH) Spill Spring 2010



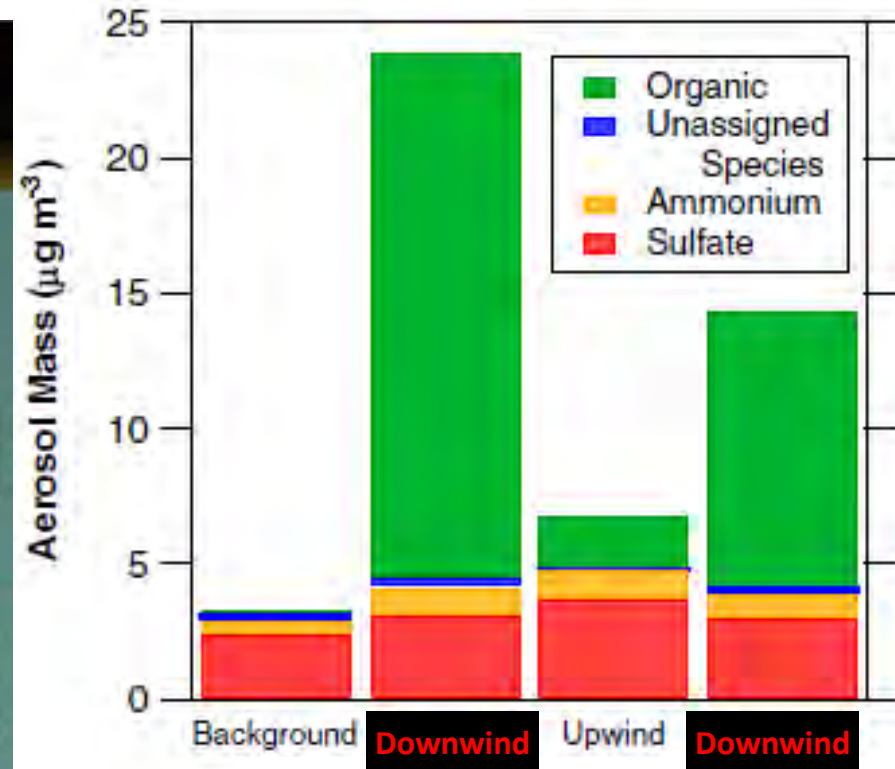
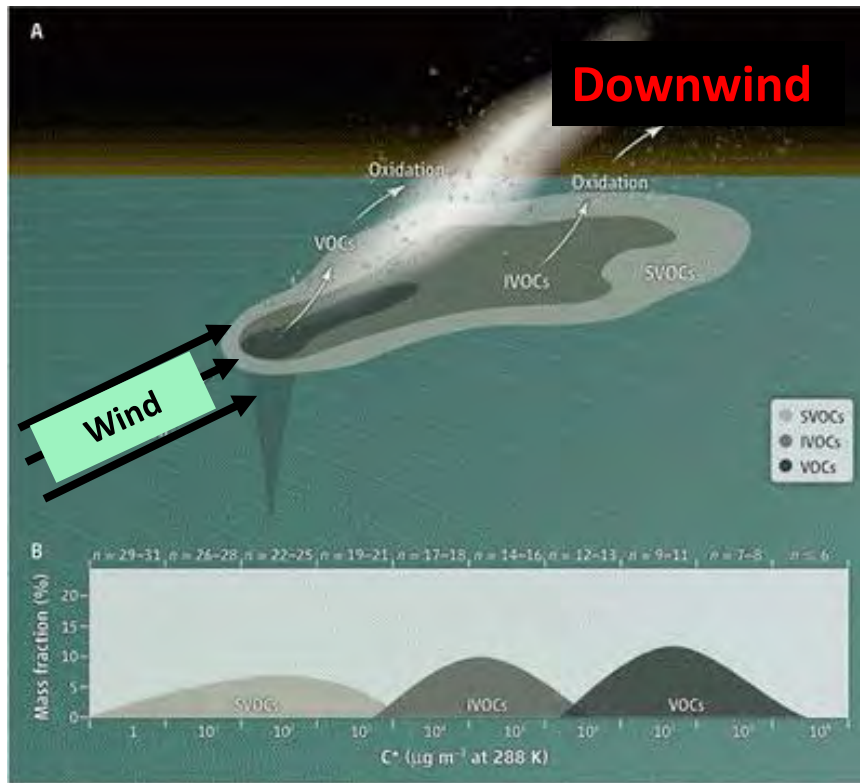
# Deepwater Horizon Spill Aerosol Formation



Middlebrook et al.

1) Aerosol formed at urban levels over DWH spill

# Deepwater Horizon Spill Aerosol Formation



Middlebrook et al.

- 1) Aerosol formed at urban levels over DWH spill
- 2) *Can oil evaporation be sufficiently modeled to predict aerosol production?*

# Atmospheric Effects of Oil Spills: Bottom-Up Evaporation Modeling

Explicit Evaporation  
Calculation

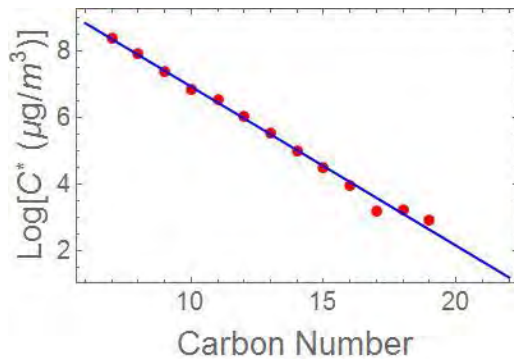
$$\frac{dM}{dt} = \sum_i \frac{K_i * P_i^{298} * \chi_i}{R * T} * e^{\Delta H_{vap,i} * \frac{1}{T} - \frac{1}{298}}$$

# Atmospheric Effects of Oil Spills: Bottom-Up Evaporation Modeling

Explicit Evaporation  
Calculation

$$\frac{dM}{dt} = \sum_i \frac{K_i * P_i^{298}}{R * T} * \chi_i * e^{\Delta H_{vap,i} * \frac{1}{T} - \frac{1}{298}}$$

Vapor Pressure

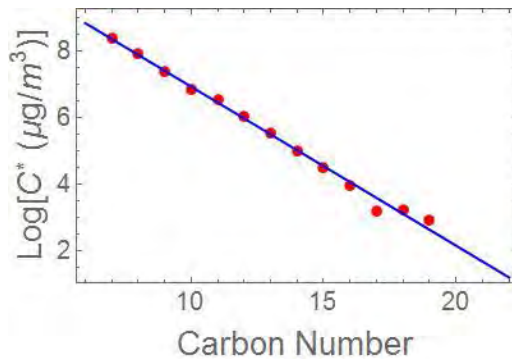


# Atmospheric Effects of Oil Spills: Bottom-Up Evaporation Modeling

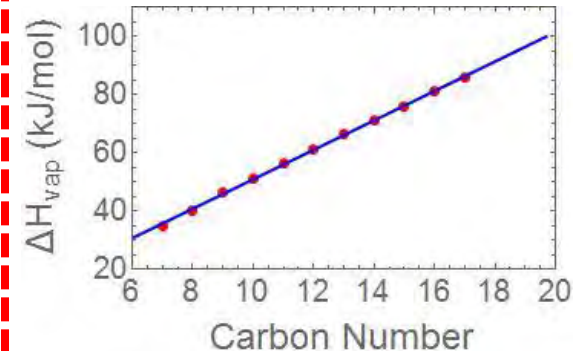
Explicit Evaporation  
Calculation

$$\frac{dM}{dt} = \sum_i \frac{K_i * P_i^{298} * \chi_i}{R * T} * e^{\Delta H_{vap,i} * \frac{1}{T} - \frac{1}{298}}$$

Vapor Pressure



Enthalpy of Vaporization

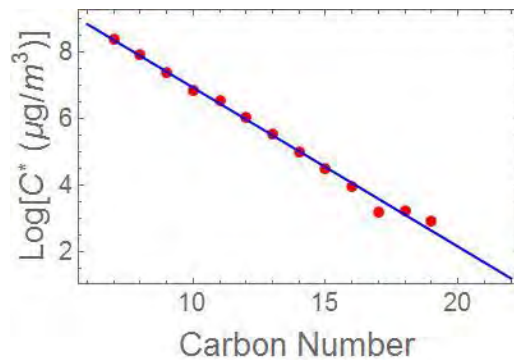


# Atmospheric Effects of Oil Spills: Bottom-Up Evaporation Modeling

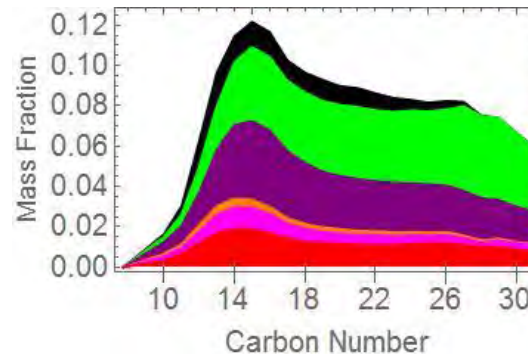
Explicit Evaporation  
Calculation

$$\frac{dM}{dt} = \sum_i \frac{K_i * P_i^{298} * \chi_i}{R * T} * e^{\Delta H_{vap,i} * \frac{1}{T} - \frac{1}{298}}$$

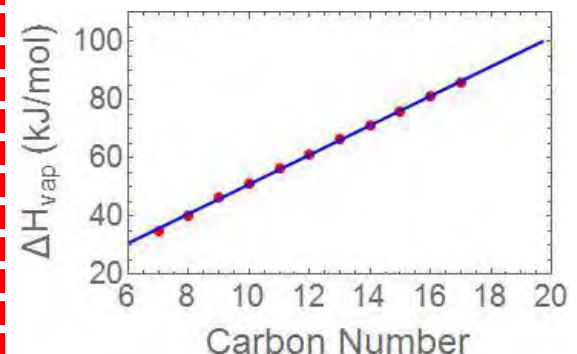
Vapor Pressure



Composition Data



Enthalpy of Vaporization

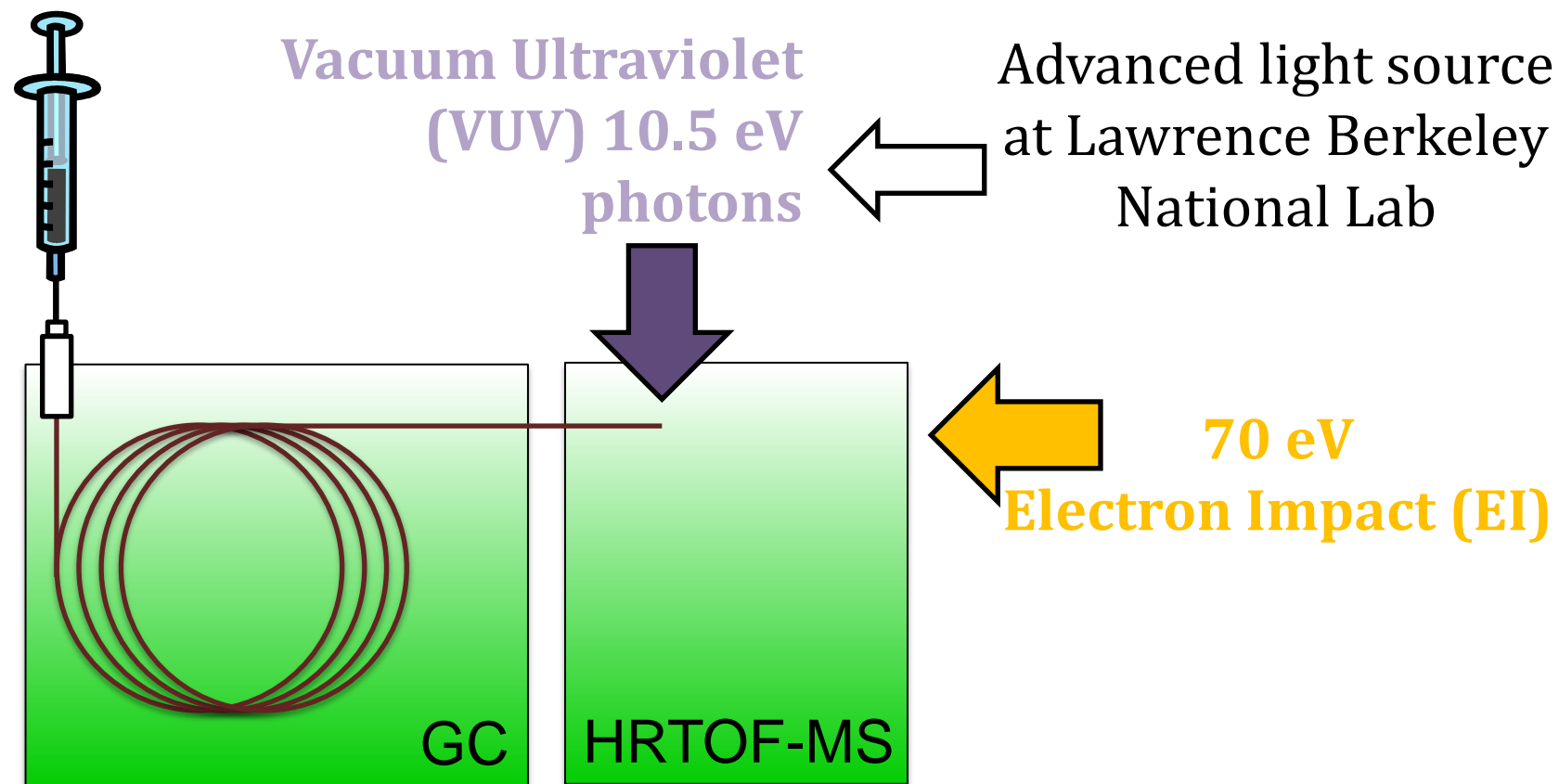


Comprehensive composition allows:

- 1) Direct calculation of evaporation
- 2) Explicit emissions for species that form air pollution

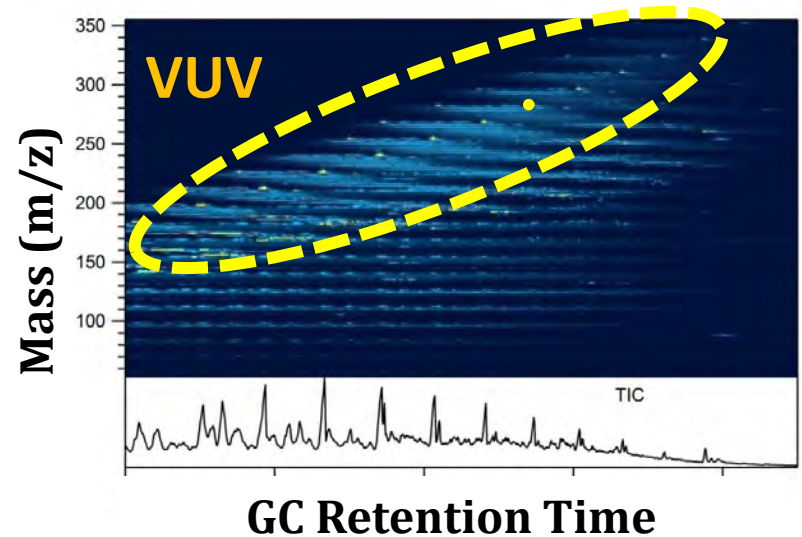
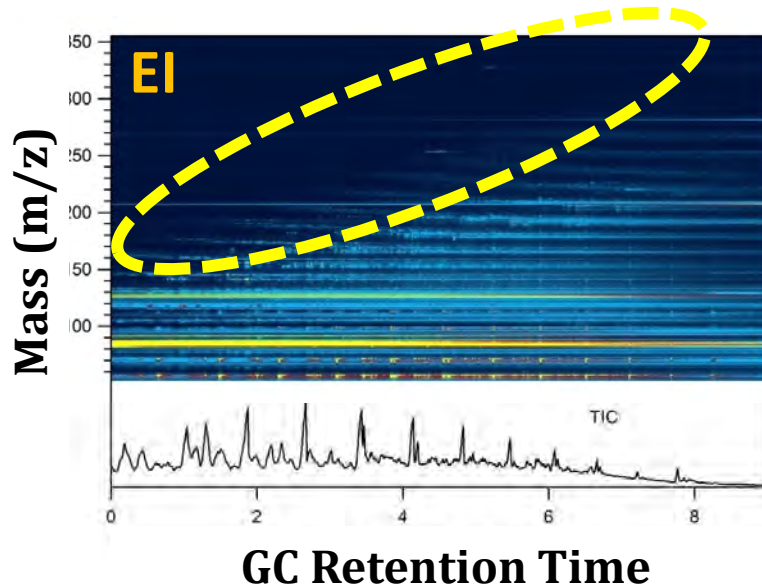
# GC-VUV-MS :

## Composition Determination of Oil



# Diesel Fuel:

## Mass Spectrum vs. GC retention time

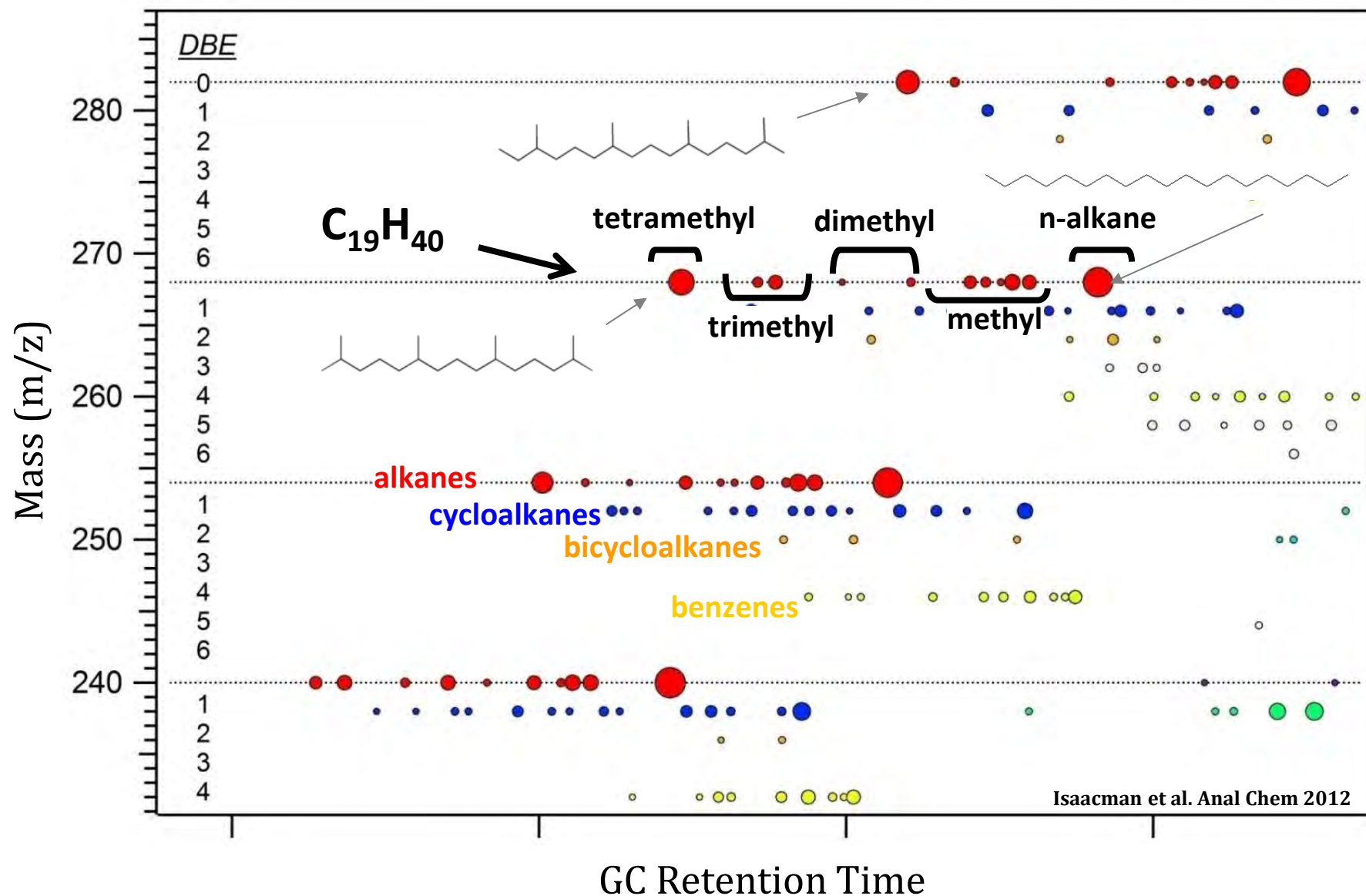


### GC-VUV-MS

Low-fragmentation

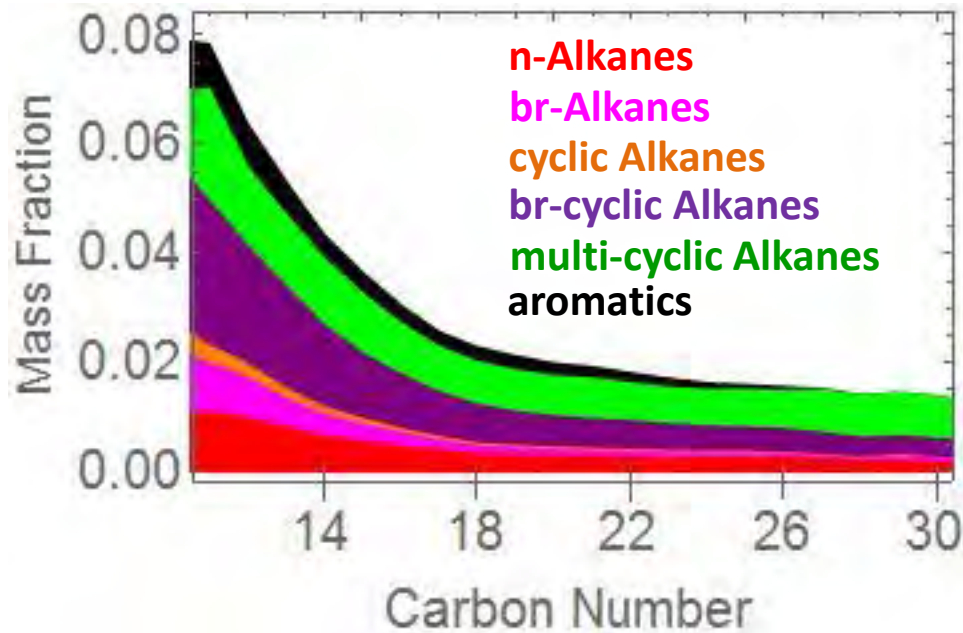
Molecular weight identifies hydrocarbons

# Crude Oil Composition: Branching



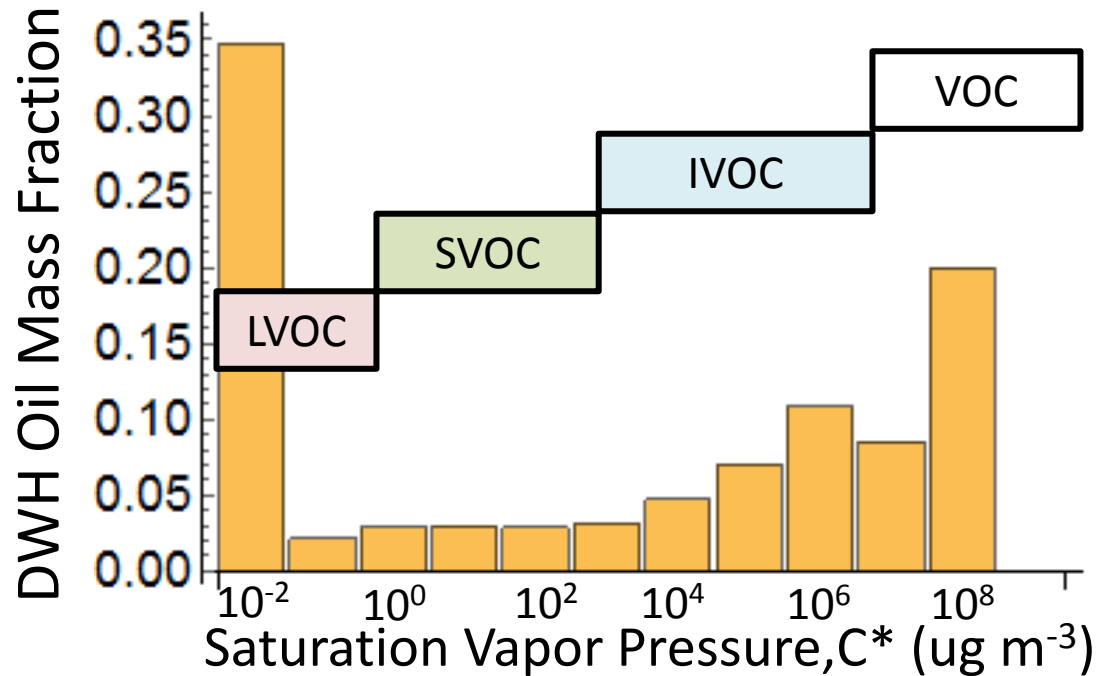
# Crude Oil Composition

## Gulf of Mexico: Light Crude



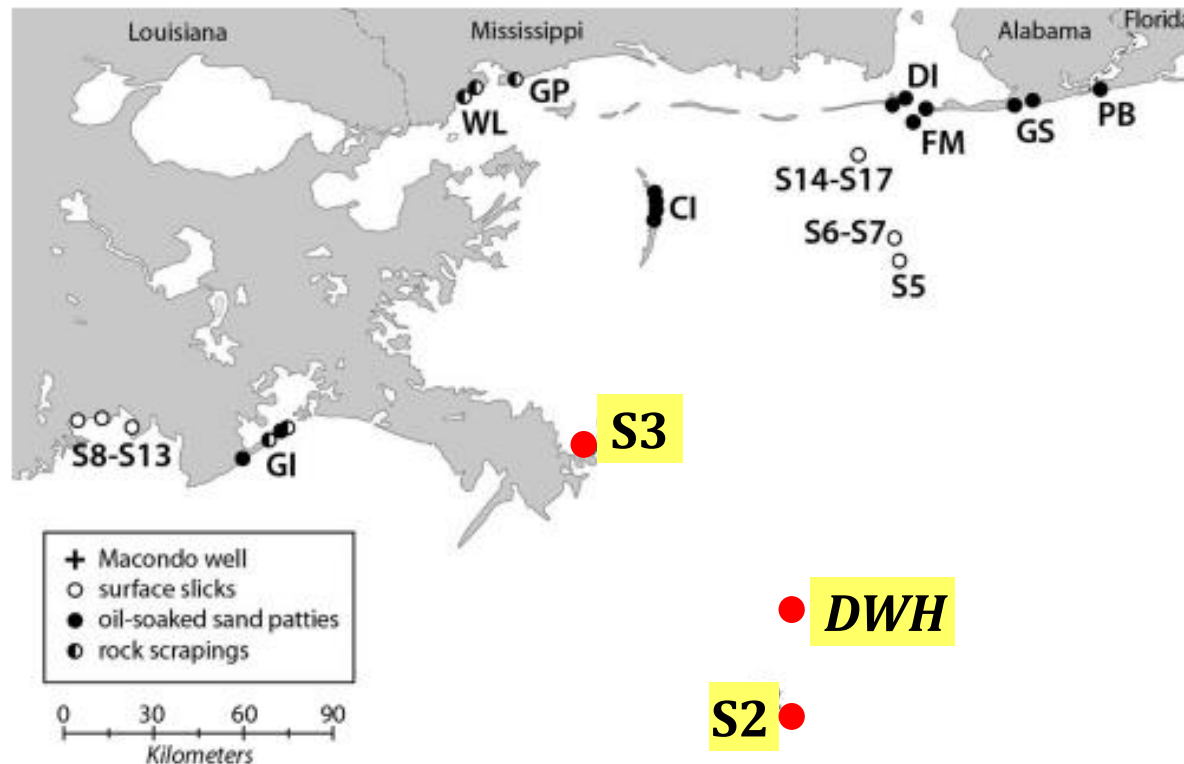
- 1) *Each compound* in oil is classified by:
  - i. carbon number,
  - ii. number of cyclic rings
  - iii. aromaticity
  - iv. degree of branching
- 2) *These are the key features needed to predict volatility and aerosol production.*

# Crude Oil Volatility



- 1) DWH components span the full range of volatilities
- 2) SOA formation potential of evaporating liquids depends both evaporation rate and SOA yield, both related to vapor pressure

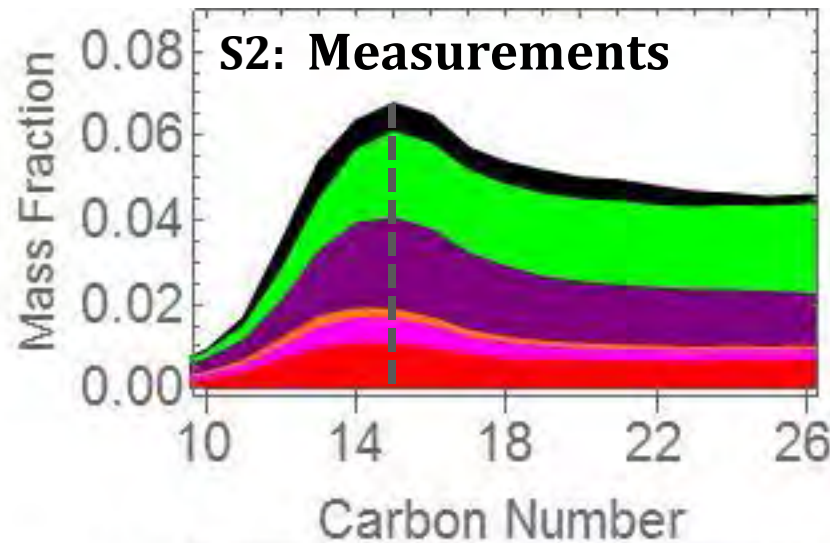
# Surface Samples From *DWH* Spill: Locations and Descriptions



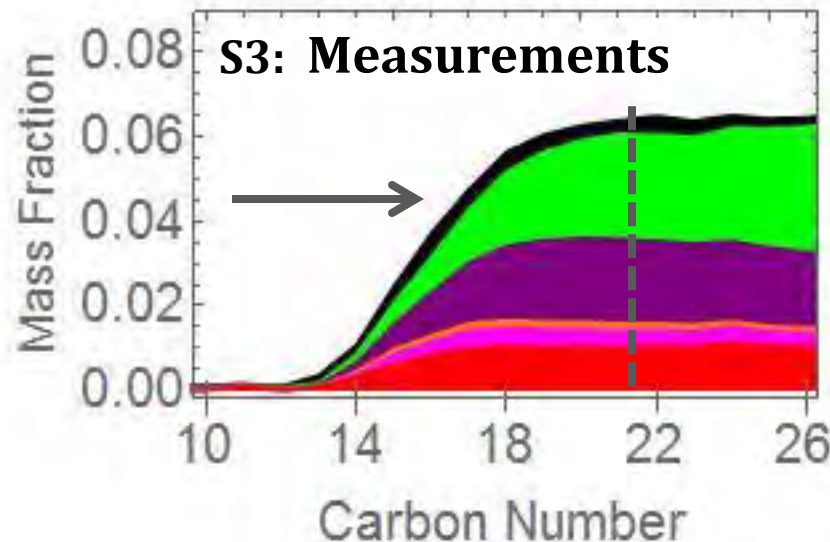
Aeppli et al. 2012

Sample	Type	Location	Approximate Surface Transit Time
S2	Fresh-slick	36km South	1 day
S3	Aged-slick	130km Northwest	5 days

# Surface Sample Distributions: Measurements for S2 and S3



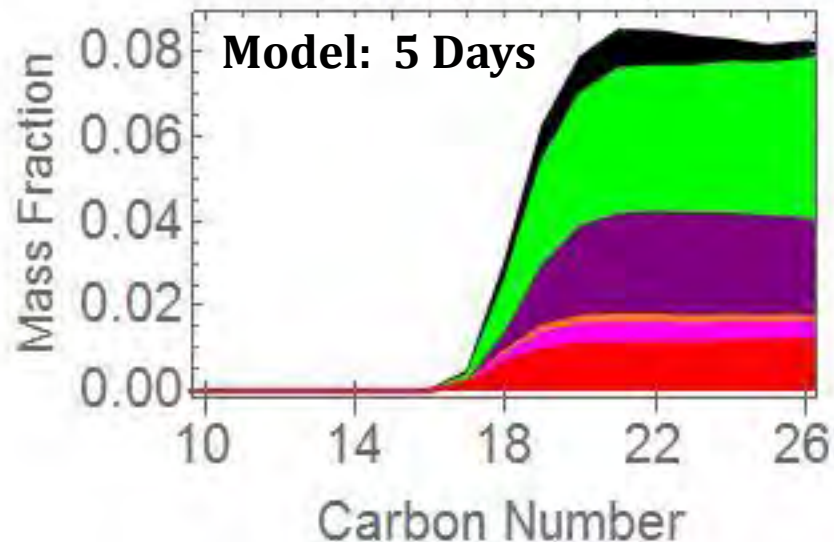
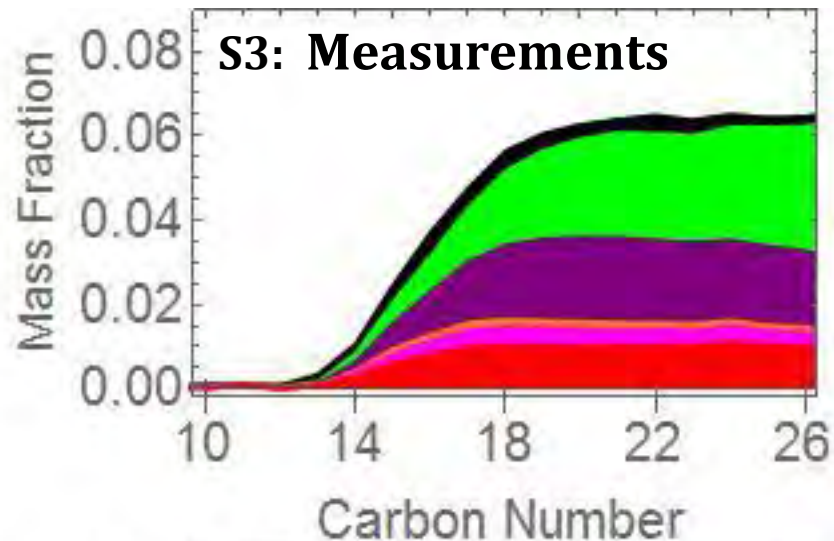
aromatics  
multi-cyclic Alkanes  
br-cyclic Alkanes  
cyclic Alkanes  
br-Alkanes  
n-Alkanes



- 1) S2 and S3: both surface slick samples
- 2) Change in S3 composition shows evaporation

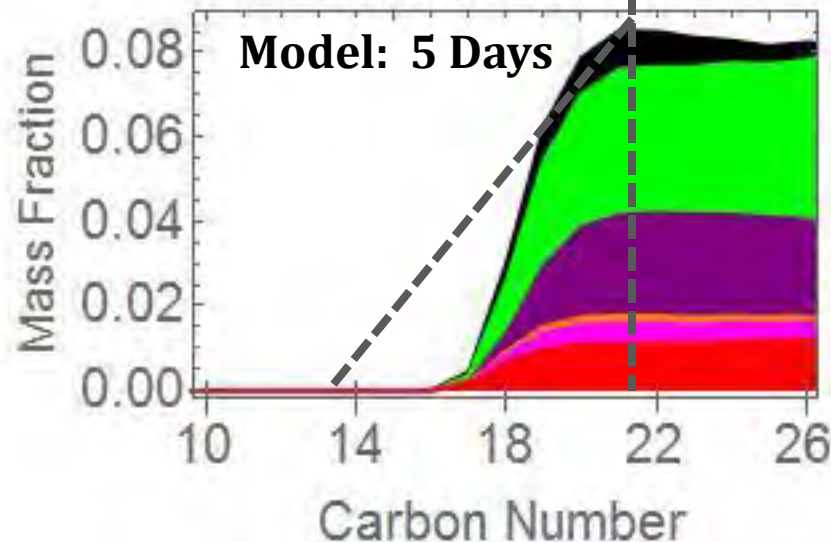
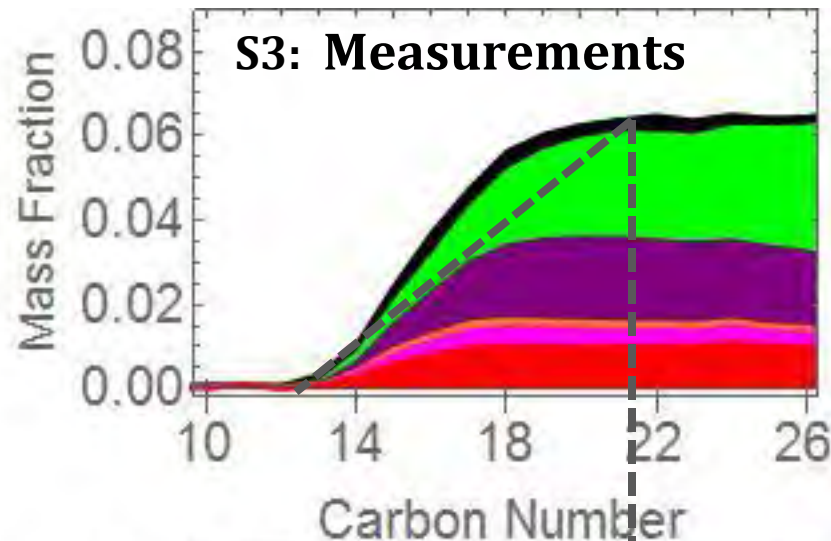
# Measurement vs. Predictions

## 5 Days Evaporative Aging of DWH Oil



# Measurement vs. Predictions

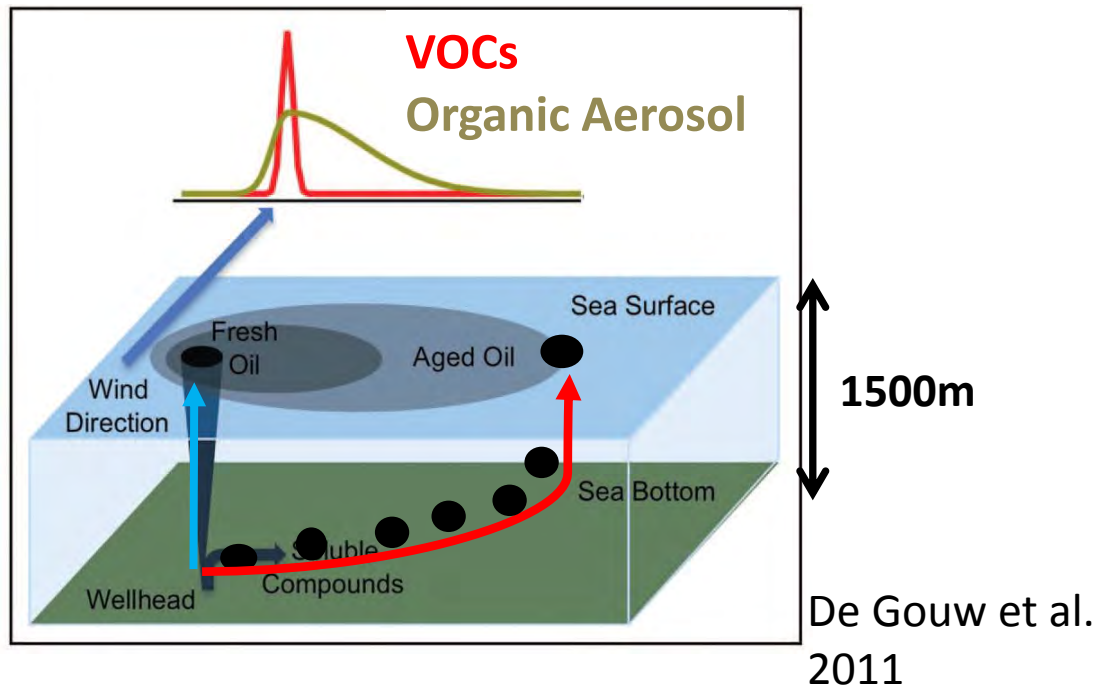
## 5 Days Evaporative Aging of DWH Oil



a) Peaks of distributions match, but the *leading edges* do not match

b) Model results show the oil did not follow simple surface transport

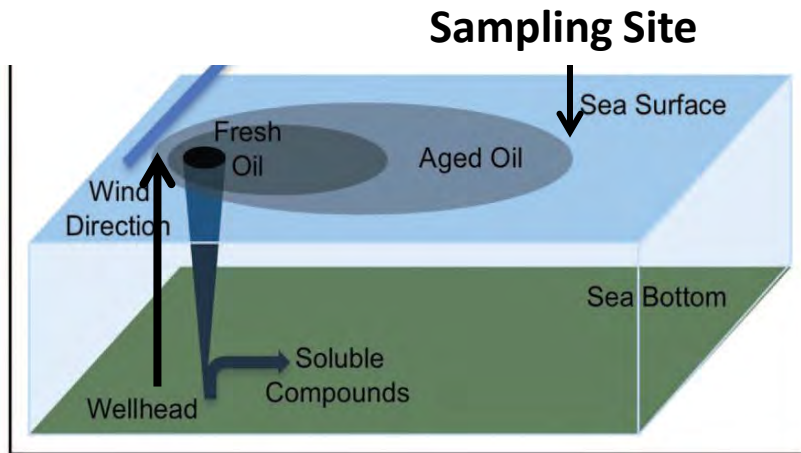
# Surfaced Oil Has Multiple Transport Histories



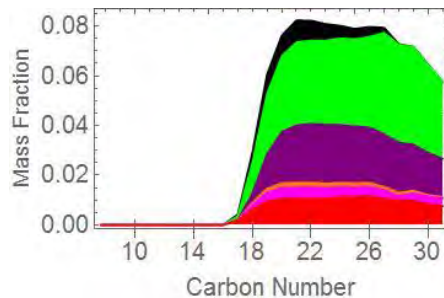
- 1) Sub-surface transport prevents evaporation
- 2) Evaporative age of surface oil affects emissions and pollutant formation

# Surface Samples

## Basis Set of Evaporative Ages

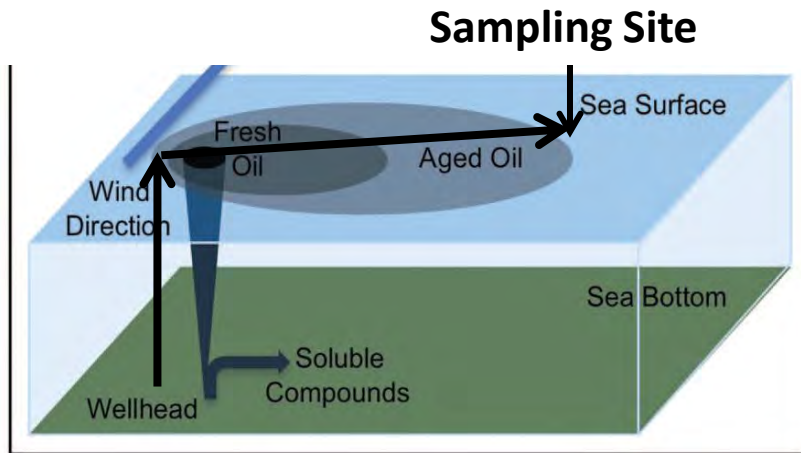


**c1**

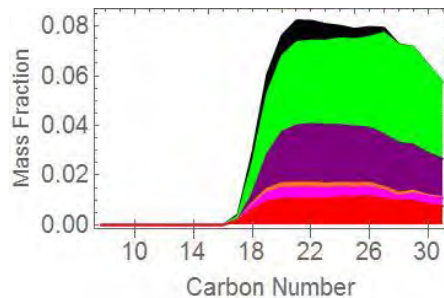


# Surface Samples

## Basis Set of Evaporative Ages

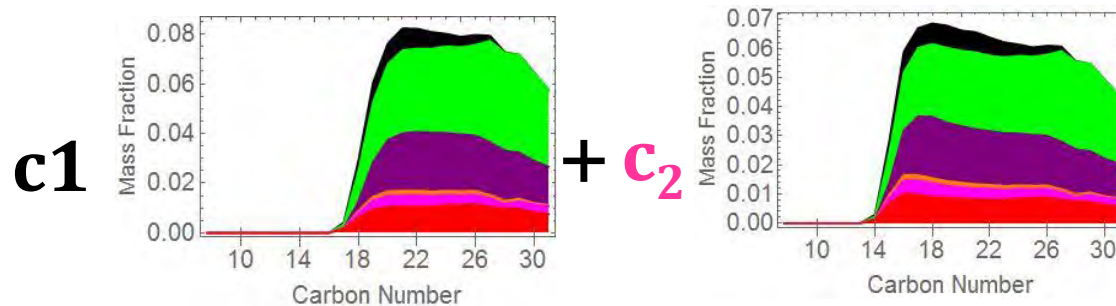
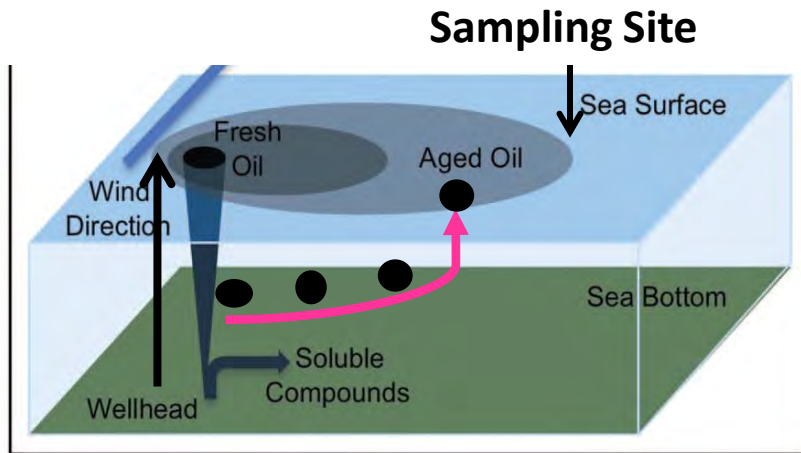


**c1**



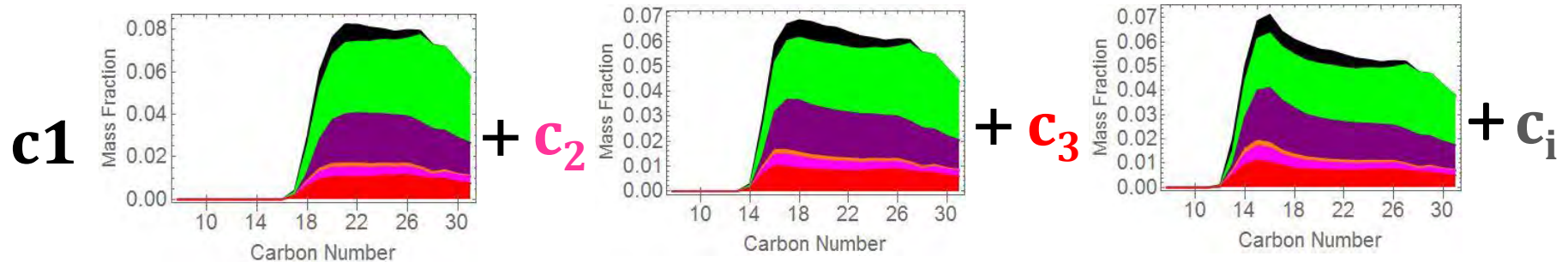
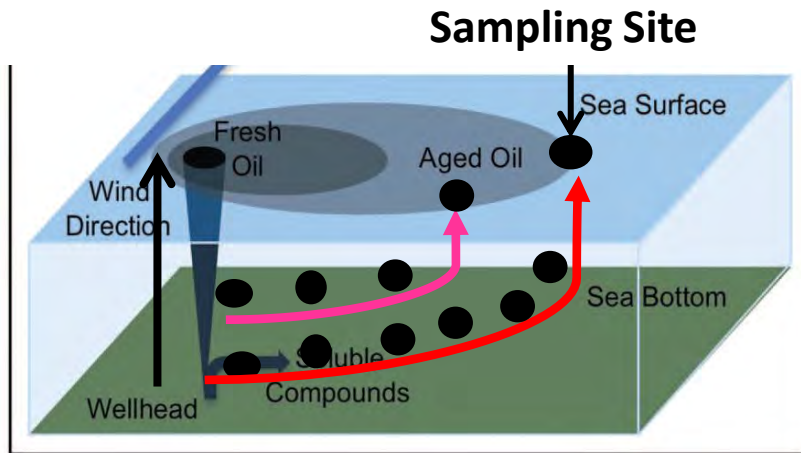
# Surface Samples

## Basis Set of Evaporative Ages



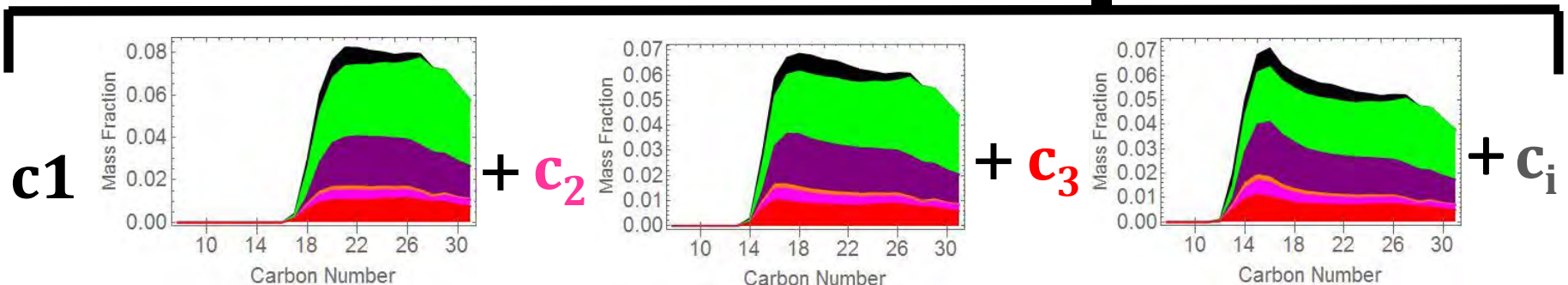
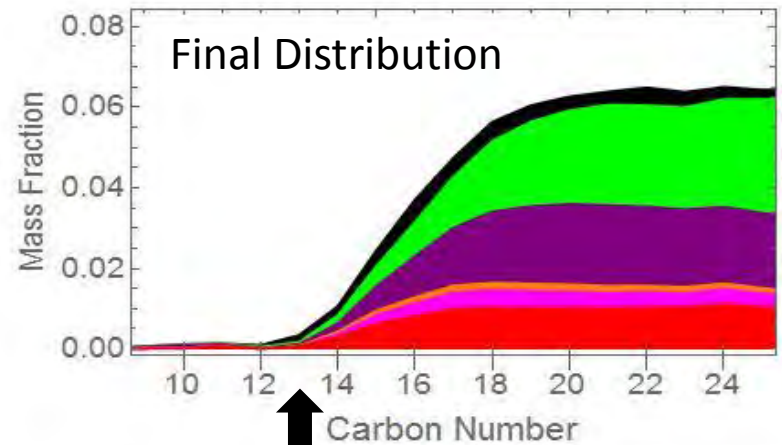
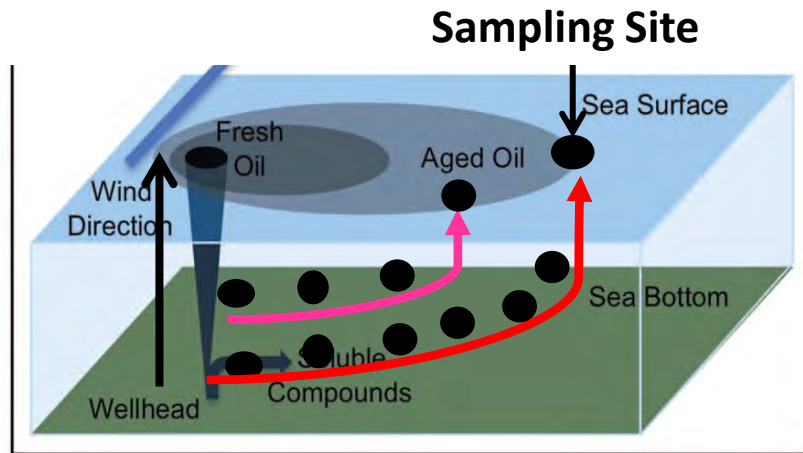
# Surface Samples

## Basis Set of Evaporative Ages



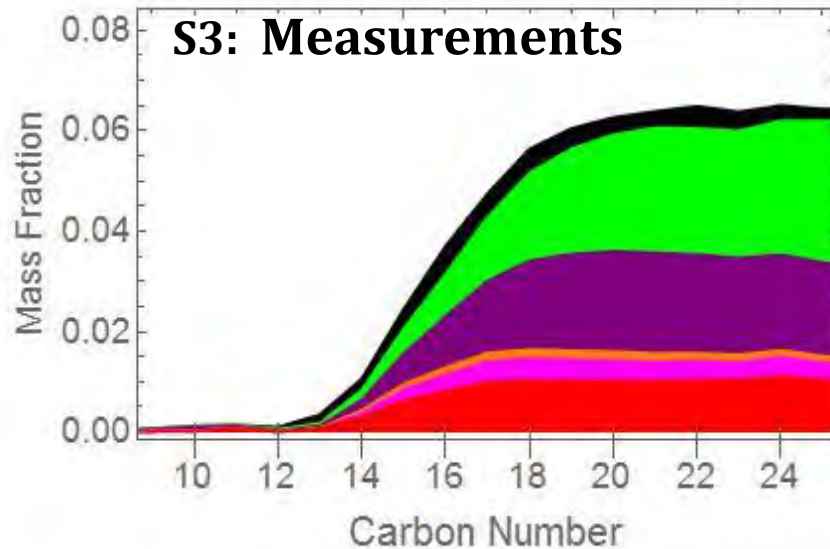
# Surface Samples

## Basis Set of Evaporative Ages

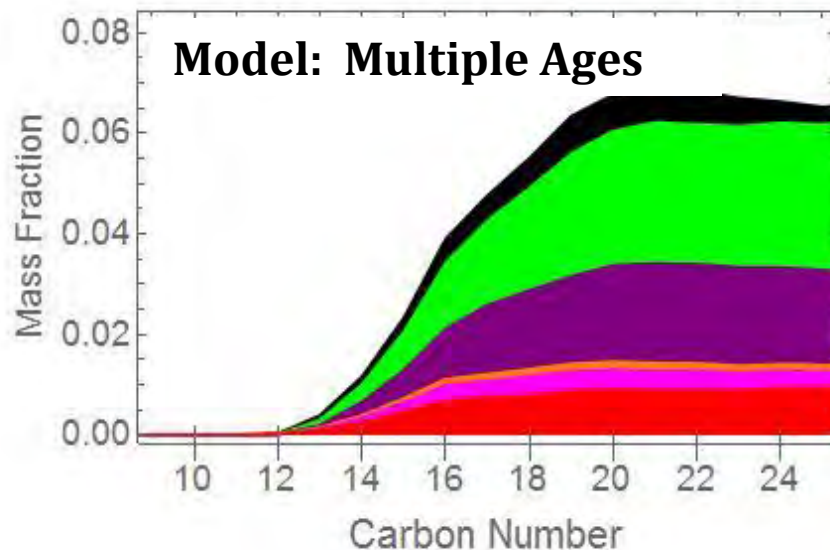


The final measured distribution can be fit from a basis set of distributions with a range of evaporative ages

# Measurements vs. Model: Range of Evaporative Ages

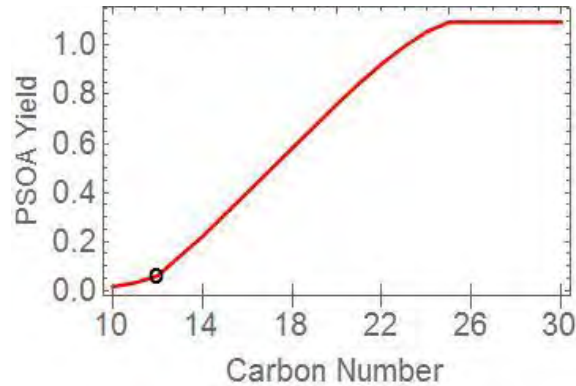


The measured composition can be fit by combining oil with different evaporative ages.

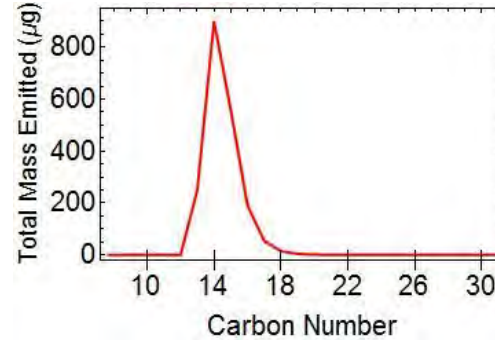


Evaporative Age	Fraction of Final Oil
0.5-1.5 days.	80%
4.8 days.	20%

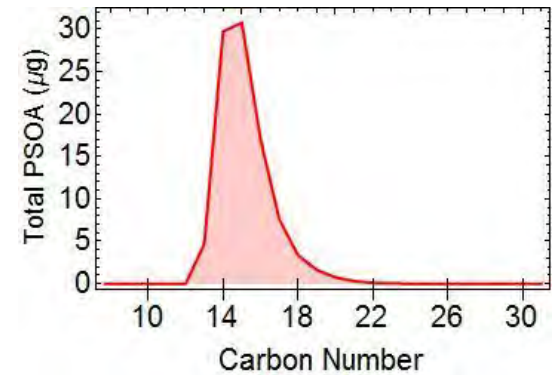
# Predicting Potential Pollutant Formation



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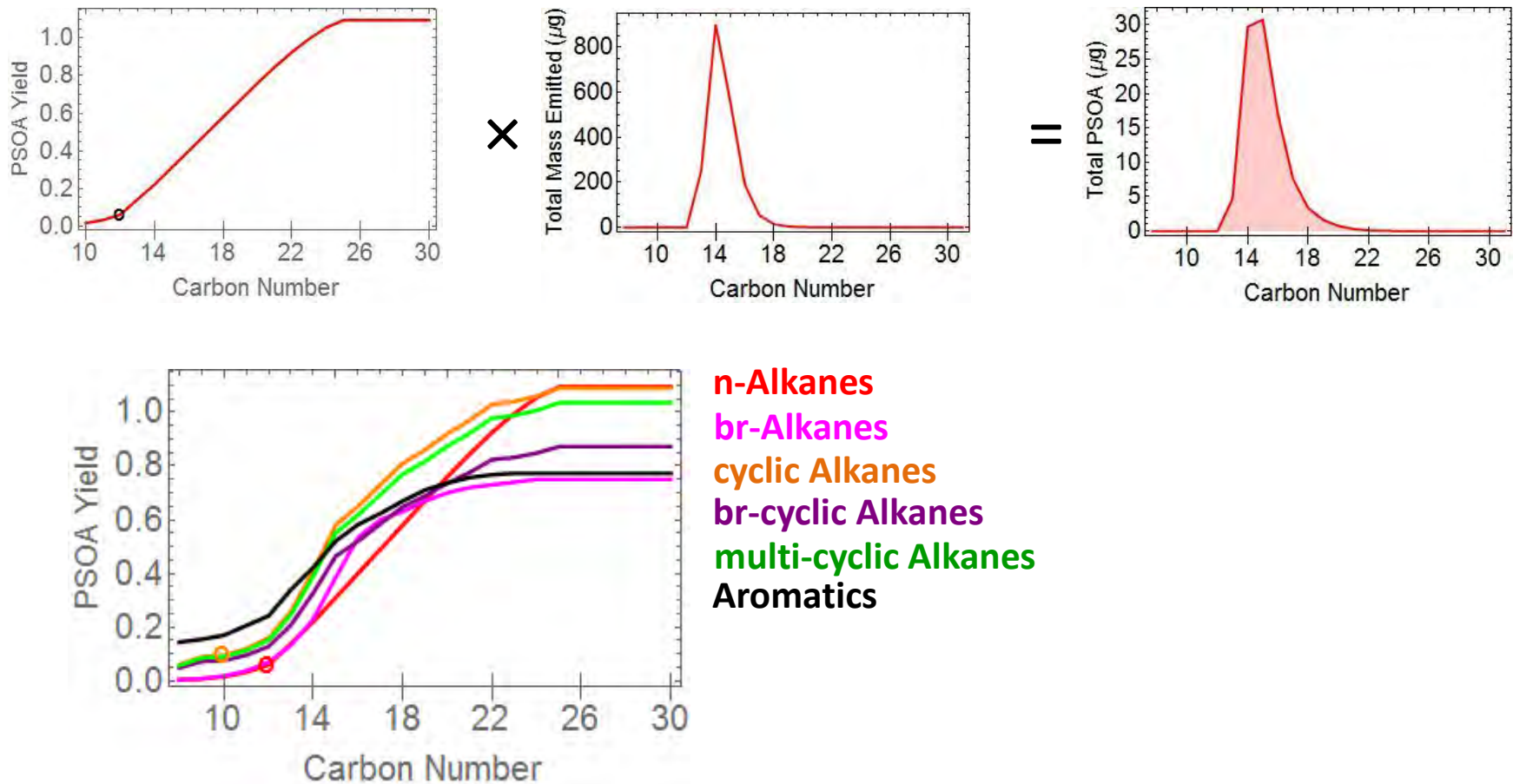


Low-NO<sub>x</sub> P-SOA Yield Estimates

Evaporative Oil Emissions

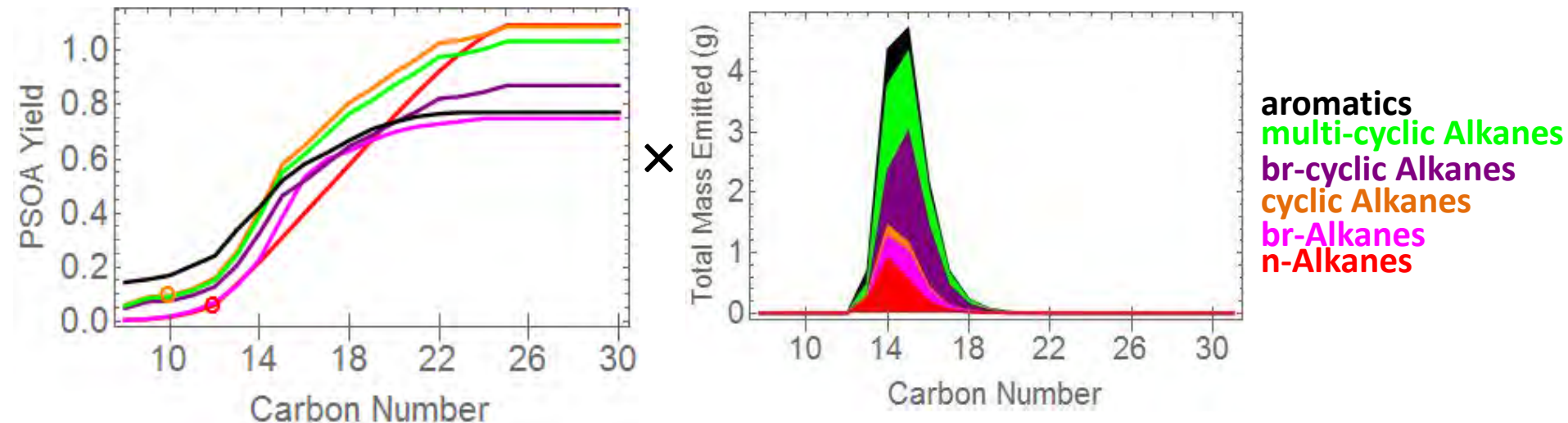
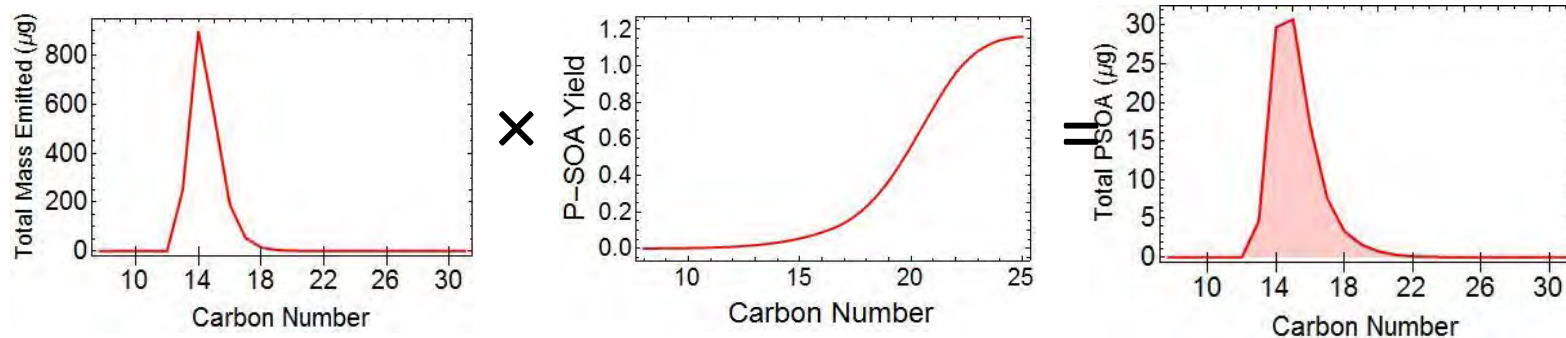
P-SOA Mass Formed

# Predicting Potential Pollutant Formation



SOA yields utilize current SOA parameterizations (Gentner 2012, Jathar 2014, Zhang 2014) and available Low-NO<sub>x</sub> yield measurements for IVOC (Cappa 2013, Tkacik 2012)

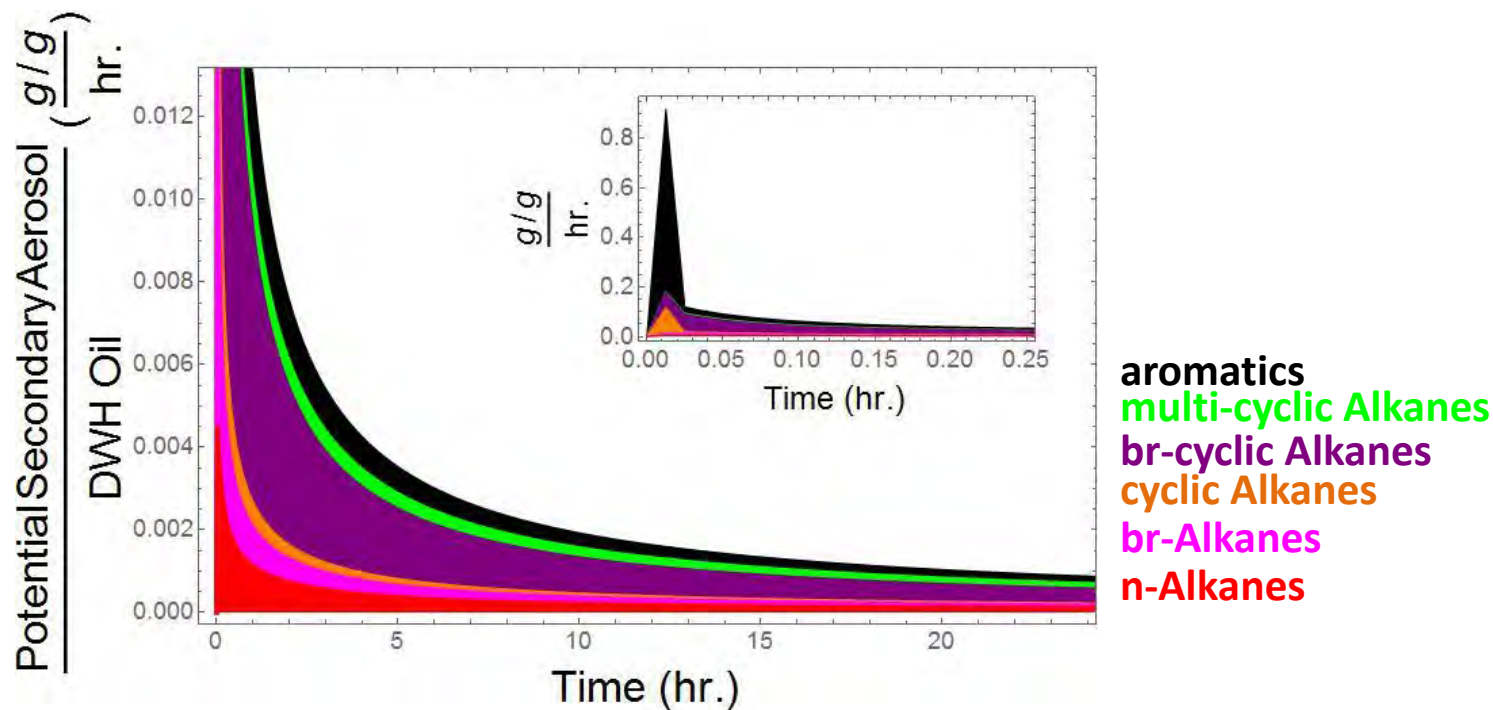
# Predicting Potential Aerosol Formation



- 1) IVOCs are important SOA precursors
- 2) Experiments needed for a wider range of chemical structures (cyclics)
  - Same compound classes critical for vehicular emissions (e.g. diesel trucks)

# Predicting SOA

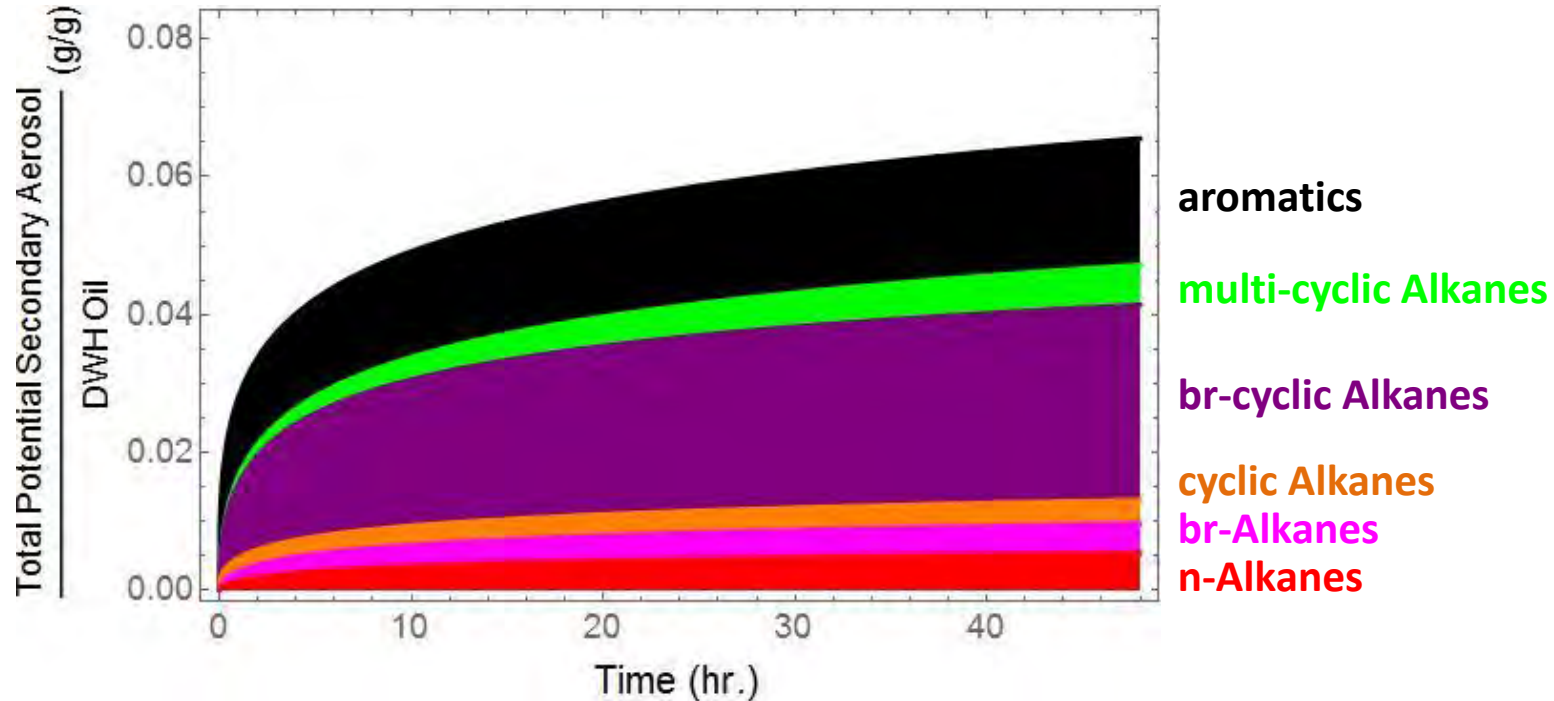
## Changing Dominant Precursor Emissions



- 1) Initial SOA precursor flux (<1 hr.) : **Aromatics** dominate
- 2) Sustained SOA precursor flux: **branched-cyclic alkanes** dominate

# Predicting SOA

## Total Aerosol Production

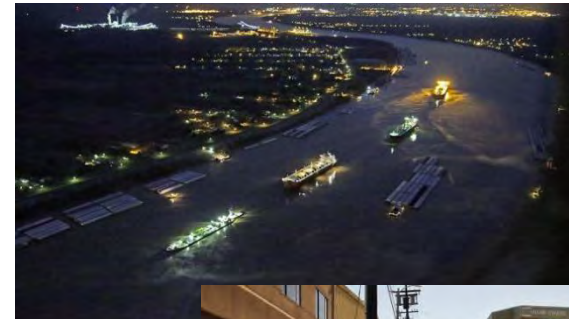
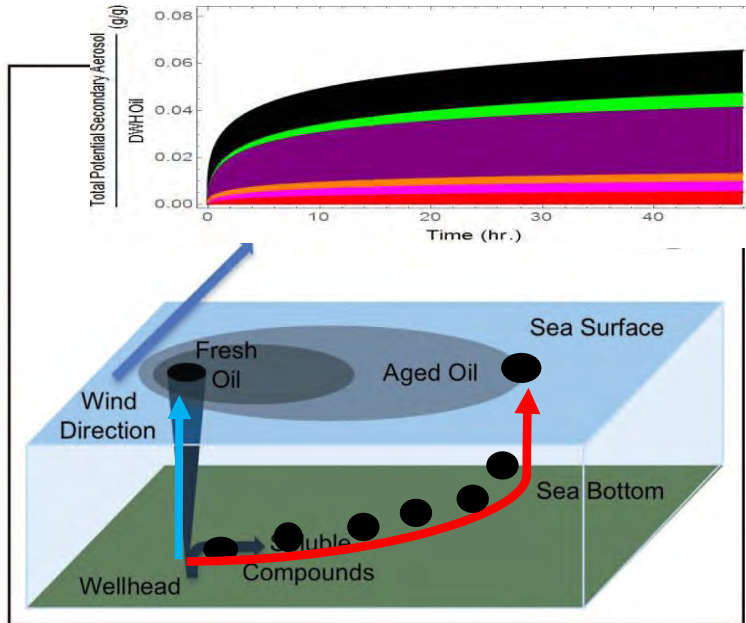


- 1) Total potential SOA yield is 6.5% for evaporative oil emissions over 2 days  
Observation-based estimates were 8% (+/-4) 3 hr. downwind (~45 km) of DWH site  
IVOCs accumulate as the plume travels over the aged slick
- 2) **IVOCs are important SOA precursors**

# Conclusions:

*Predicting how/where oil travels*

*Predicting Aerosol Formation*



Composition measurements with evaporation modeling constrain:

- 1) Where and how oil travels*
- 2) How much SOA will form in a particular location*

Predicting aerosol production from oil spills is critical for assessing health effects